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(54) Title: MIXED CHROMIUM CATALYSTS AND POLYMERIZATIONS UTILIZING SAME**(57) Abstract**

Mixed catalyst compositions comprised of a first supported chromium-containing catalyst component and a second supported chromium-containing catalyst component and which additionally have one or more metallic or non-metallic catalytic agents associated therewith are provided. The additional metallic or non-metallic elements associated with the catalyst components can be aluminium, titanium, zirconium, boron, phosphorous or combinations thereof. The pore volume of the silica supports used for the first and second catalyst components differs by at least 0.3 cc/g. The mixed catalyst compositions of the invention are useful for the preparation of polyolefins. They are particularly useful of polymerization of ethylene in particle form polymerizations to produce high density polyethylene blow molding resins having good processability and physical properties. The improved particle form polymerizations process and products obtained thereby using the above-described mixed catalyst compositions are also described.

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MIXED CHROMIUM CATALYSTS
AND POLYMERIZATIONS UTILIZING SAME

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This invention relates to improved catalyst compositions and processes for utilizing same. The mixed chromium catalysts are useful for polymerizing olefins and, more particularly, for use in particle form polymerizations for the manufacture of high density polyolefin resins which exhibit high resistance to environmental stress cracking and which are useful for the production of blow molded articles. More specifically, the mixed catalysts are comprised of a first and second chromium-containing supported catalyst component wherein the supports used for said first and second catalyst components have different pore volumes and wherein at least one of the catalyst components contains an additional element selected from aluminum, titanium, zirconium, boron or phosphorus.

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In the selection and production of resins for the manufacture of blow molded goods, more so than with other fabrication methods, a careful balance must be struck between the physical properties of the solid resin and the processing characteristics of the resin melt if efficient production of durable molded articles is to be achieved. While many resins have superior physical properties, they do not have acceptable rheological (viscoelastic) properties under conditions of flow and shear such as are encountered during blow molding. Conversely, other resins which exhibit satisfactory viscoelastic behavior are deficient in one or more essential physical characteristics. For this reason there is a

-2-

1 continuing effort to develop resins which have an
optimal balance of physical and rheological
properties. This is especially true with polyethylene
resins used for the manufacture of blow molded
5 bottles.

Improved processability of polyolefin
resins, i.e., improved flow properties and shear
response, is obtained by increasing the molecular
weight distribution of polymers. This has been
10 accomplished by blending separately prepared polymers
of different molecular weights and by utilizing
catalyst systems capable of directly producing
polymers having broadened molecular weight
distributions. U.S. Patent Nos. 3,959,178 and
15 4,025,707, for example, disclose the preparation of
ethylene homopolymers and copolymers of broadened
molecular weight obtained utilizing a mixed catalyst
comprising several portions of the same or different
chromium components and metal promoted variations
20 thereof wherein each portion is activated at a
different temperature. U.S. Patent Nos. 4,540,757 and
4,560,733 utilize milled blends of at least two
different silica-containing components having
different melt index potentials for the preparation of
25 titanium-containing catalysts components.

U.S. Patent No. 4,263,422 discloses
polymerizing α -olefins utilizing dual independently
supported catalysts one of which is an inorganic
halide supported titanium and/or vanadium Ziegler type
30 catalyst while the other is an inorganic oxide
supported chromium-containing catalyst.

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-3-

1 While it has been possible to improve
processing characteristics in this manner, any
processing advantage has heretofore been offset in
large part by a corresponding decrease in one or more
5 essential physical properties. For example, while the
products obtained in accordance with U.S. Patent No.
4,025,707 have good die swell characteristics and
acceptable environmental stress crack resistance and
flow properties, polymer densities are too low to
10 provide the necessary stiffness for blown bottles. On
the other hand, polymers such as those produced using
the catalysts of U.S. Patent No. 4,560,733 have
sufficiently high densities (0.960 and higher) but
typically are deficient in their resistance to
15 environmental stress cracking.

For blow molding bottles, the resin must
have sufficiently high density and high resistance to
environmental stress cracking in addition to having
acceptable processing characteristics. A density of
20 at least 0.957 is necessary to obtain the high degree
of stiffness required by molders. It is considered
even more desirable for the resin to have a density of
0.958 to 0.961. Stiffness imparts strength to bottles
and also makes thinner wall constructions possible.
25 More units can thus be produced per pound of resin,
generally referred to within the industry as
"lightweighting", which represents an economic
advantage for the processor. Lightweight resins must
also exhibit a high degree of resistance to cracking
30 under environmental stress, that is, while being
stretched or bent in several directions at once.

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-4-

1 While stiffness increases with density as
noted above, an inverse relationship exists between
density and resistance to environmental stress
cracking. As density is increased, resistance to
5 environmental stress cracking is reduced. Both of the
above relationships assume that the melt index of the
resins are the same or essentially the same. A
balance must therefore be struck between the density,
i.e., stiffness, of the resin and the resistance of
10 the resin to environmental stress cracking.

 It would be advantageous if the molecular
weight distribution of polymers would be varied and if
polyethylene resins having an optimal balance of
rheological and physical properties could be produced.
15 It would be even more desirable if high density resins
having high resistance to stress cracking useful for
the manufacture of blown bottles could be obtained
utilizing mixtures of known catalyst components.
These and other advantages are realized using the
20 mixed catalyst compositions of the present invention
which are described in detail to follow.

 The present invention relates to a mixed
chromium catalyst composition containing a first and
second silica-supported chromium catalyst component;
25 said first and second catalyst components present at a
weight ratio from 10:1 to 1:10 and each containing
from 0.1 to 2.0 weight percent chromium with at least
one of said catalyst components containing an
additional metallic or non-metallic element selected
30 from aluminum, titanium, zirconium, boron or
phosphorus with the proviso that when one of the
catalytic components contains chromium and aluminum

-5-

1 the other component shall contain more than one
metallic or non-metallic catalytic element; and the
silica supports of said first and second catalyst
components ~~differing in pore volume by at least 0.3~~
5 cc/g. The mixed chromium catalyst compositions of the
present invention consist essentially of a first and
second silica-supported chromium catalyst component;
said first and second catalyst components present at a
weight ratio from 10:1 to 1:10 and each containing
10 from 0.1 to 2.0 weight percent chromium with at least
one of said catalyst components containing an
additional metallic or non-metallic element selected
from aluminum, titanium, zirconium, boron or
phosphorus. The silica supports of said first and
15 second catalyst components differ in pore volume by at
least 0.3 cc/g and, most usually, the pore volume of
the silica support of the first catalyst component is
greater than 1.0 cc/g.

In a particularly useful embodiment of the
20 invention the pore volume of the silica support used
for the first catalyst component is from 1.7 to 3.1
cc/g and the pore volume of the silica support used
for the second catalyst component is from 1.0 to 2.0
cc/g. The weight ratio of the first and second
25 catalyst components will more preferably range from
5:1 to 1:5 and the ~~metallic and non-metallic~~
element(s) are usually present in amounts from 0.1 to
6.0 weight percent. Especially useful mixed catalysts
of the invention contain from 2 to 4.5 weight percent
30 aluminum, titanium, or zirconium and, when a non-metal
is present, from 0.1 to 1.0 weight percent phosphorous
or boron.

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-6-

1 In another particularly advantageous
embodiment, the individual catalyst components or a
~~mixture of the catalyst components~~ are thermally
activated by heating in a non-reducing atmosphere at a
5 temperature from 450°F to 1700°F. It is even more
useful if, prior to the thermal activation, the
individual catalyst component or mixture thereof is
heated at 575°F to 1650°F in a reducing atmosphere -
preferably a mixture of nitrogen and carbon monoxide.
10 The mixed chromium compositions are effective
catalysts for the polymerization of olefins by
themselves or, as is more generally the case, in
combination with metallic or non-metallic reducing
agents such as trialkyl aluminums, alkyl aluminum
15 halides, alkyl aluminum alkoxides, dialkyl zincs,
dialkyl magnesiums, alkali metal borohydrides,
aluminum borohydrides, alkyl boranes, and boron
hydrides.

 In accordance with the present invention,
20 polyethylene resins having good processing
characteristics, high density and high resistance to
environmental stress cracking are obtained using mixed
chromium catalysts obtained by combining two or more
different supported chromium-containing catalyst
25 components. The catalyst components which are mixed
to obtain the present catalyst compositions will
differ based on the support material used and may also
differ based on the type and/or amount of catalytic
agent associated therewith. Whereas the individual
30 chromium-containing catalyst components may be known,
it has unexpectedly been discovered that by combining
certain of these catalyst components in specific

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-7-

1 ratios the resulting mixed catalysts yield resins
which, in addition to having excellent processing
characteristics by virtue of a broadened molecular
weight distribution, also have high densities and high
5 resistance to environmental stress cracking. This
balance of desirable processability with both high
density and high resistance to stress cracking makes
the resins highly useful in blow molding applications
and particularly for the production of blown bottles.

10 Polyethylene resins having densities of at
least 0.957, high environmental stress cracking
resistance (ESCR), and acceptable flow properties and
shear response are obtained using the present improved
catalyst compositions which are mixtures of first and
15 second chromium-containing silica supported catalyst
components wherein the silica supports for said
catalyst components differ in pore volumes by at least
0.3 cc/g and at least one of the catalyst components
contains an additional metallic or nonmetallic element
20 selected from aluminum, titanium, zirconium, boron or
phosphorus. These catalytic metallic and nonmetallic
elements, also referred to herein as catalytic agents,
will be deposited on and associated with the support
material in accordance with conventional practice.

25 More particularly, resins produced in accordance with
the present invention have densities from 0.958 to
0.961 and ESCR values greater than 8 hours and, more
preferably, greater than 10 hours. ESCR values
referred to herein are bottle ESCR F50 values as
30 determined in accordance with ASTM D-2561, Procedure C
(modified), unless otherwise indicated.

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-8-

1 In addition to having densities and bottle
ESCRs within the above-specified ranges, the resins
also typically have ~~melt indexes (pellet)~~ from 0.1 to
0.7 and, more particularly, in the range 0.2 to 0.4
5 and melt index ratios (MIRs) in the range 60 to 180
and, more preferably, 80 to 125. MIR is generally
considered to be an approximation of molecular weight
distribution and is the ratio between the high load
melt index (HLMI) determined in accordance with ASTM
10 D1238-57T, condition F, and the MI determined in
accordance with ASTM D1238-57T, condition E. In
general, with resins of comparable MI, polymers with
broader molecular weight distributions have higher
MIRs and better flow properties than their lower MIR
15 counterparts.

 While it is generally recognized that
rheological properties can be modified by varying the
support material used for a particular catalyst and
that the melt index is affected by the pore volume of
20 the silica support, it is unexpected the above-
described highly desirable balance of rheological and
physical properties can be obtained by the use of
mixed catalysts based on two different chromium-
containing components. Heretofore, any processing
25 advantages which have been realized were generally
accompanied by a corresponding undesirable reduction
in density and/or ESCR.

 The catalyst compositions of the present
invention are mixtures of two discreet supported
30 catalyst components present in defined ratios. Both
catalyst components employed for the improved mixed
catalyst compositions of the invention necessarily

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-9-

1 have chromium on a support. Additionally, one or both
of the catalyst components may also have other
metals/nonmetals deposited thereon.

5 Silica is utilized as the support for the
two catalyst components, however, the silica employed
for the first catalyst component and the silica used
for the second catalyst component will differ in pore
volumes by at least 0.3 cc/g. The weight ratio of the
10 first and second supported catalyst component in the
mixture ranges from 10:1 to 1:10 and, more preferably,
from 5:1 to 1:5. In a particularly useful embodiment
the weight ratio of the two catalyst components
comprising the mixture is from 3:1 to 1:3.

15 The silica support employed for the first
catalyst, referred to herein as the higher pore volume
support, will have a pore volume greater than 1.0
cc/g. This higher pore volume support more usually
has a pore volume of 1.7 cc/g or above and in a
particularly useful embodiment the pore volume is
20 greater than 2.0 cc/g. In general, the pore volume
will not exceed about 3.1 cc/g. Silica supports of
this type are well known and can be obtained in
accordance with known procedures. For example, silica
xerogels having the prescribed pore volumes are
25 described in U.S. Patent Nos. 3,652,214, 3,652,215 and
3,652,216, details of which are incorporated herein by
reference.

30 Especially useful high pore volume silicas
for the catalysts of this invention have pore volumes
from 2.1 cc/g to 2.9 cc/g. These high pore volume
materials typically have surface areas in the range

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-10-

1 100 to 800 m²/g and, more preferably, in the range 200
to 500 m²/g.

5 ~~The silica support employed for the second~~
catalyst component, referred to herein as the lower
pore volume support, will have a pore volume at least
0.3 cc/g less than the higher pore volume support
employed for the first catalyst component. In
10 general, the pore volume of these silicas can range
from 0.3 to 2.6 cc/g but, more usually, will range
from 1.0 to 2.0 cc/g. It is particularly advantageous
if the second catalyst component is supported on a
silica support having a pore volume from 1.5 cc/g to
1.9 cc/g.

15 While granular silica supports are most
commonly used, microspheroidal silicas can be
advantageously utilized as the support material for
either or both catalyst components. Silica xerogels
of this later type are obtained by conventional
methods known to the art such as described in U.S.
20 Patent No. 3,453,077, and are commercially available
from Davison Chemical Division, W.R. Grace & Co.,
under the designation MS-952. Microspheroidal silica
of pore volume 1.6 cc/g to 1.8 cc/g is most
advantageously employed as the lower pore volume
25 support for the second catalyst component.

30 Either or both of the silica supports can be
calcined prior to having the metal deposited thereon.
If calcining is employed prior to deposition, it can
be carried out at temperatures ranging from about
200°F to about 1800°F in accordance with conventional
procedures. In one particularly useful embodiment of
the invention the higher pore volume silica support

-11-

1 used for the first catalyst component is calcined
before deposition.

Known chromium-containing compounds capable
of reacting with the surface hydroxyl groups of the
5 silica supports can be utilized to effect deposition
of the chromium thereon. Examples of such compounds
include chromium nitrate, chromium trioxide,
organochromium compounds, including chromocene,
chromate esters such as chromium acetate, chromium
10 acetylacetonate and t-butyl chromate, silyl chromate
esters, phosphorus-containing chromate esters, and the
like.

When an additional catalytic agent, metal or
nonmetal, is present on either the first or the second
15 catalyst component it can be deposited in the
conventional manner. For example, a compound of the
metal or nonmetal can be included with the chromium
compound during the chromium deposition or, after the
chromium deposition is complete, any additional
20 catalytic agents can be deposited in a separate step.
It is also possible to utilize a chromium compound or
complex containing additional catalytic elements.
This latter procedure is especially useful where
phosphorus or boron are to be deposited on either the
25 first or second catalyst component. Most notable in
this regard is the use of organophosphoryl chromium
compounds of the type disclosed in U.S. Patent No.
3,985,676.

Known aluminum-containing compounds capable
30 of reacting with the surface hydroxyl group of the
silica supports can be employed to deposit the
aluminum thereon. Examples of such aluminum compounds

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-12-

1 include aluminum alkoxides, such as aluminum sec-
butoxide, aluminum ethoxide, aluminum isopropoxide;
alkyl aluminum alkoxides, such as ethyl aluminum
ethoxide, methyl aluminum propoxide, diethyl aluminum
5 ethoxide, diisobutyl aluminum ethoxide, etc.; alkyl
aluminum compounds, such as triethyl aluminum,
triisobutyl aluminum, etc.; alkyl or aryl aluminum
halides, such as diethyl aluminum chloride; aryl
aluminum compounds, such as triphenyl aluminum;
10 aryloxy aluminum compounds, such as aluminum
phenoxide; and the like. While the aluminum may be
deposited on either the first or second component of
the mixed catalyst, it is preferably associated with
the first catalyst component and supported on the high
15 pore volume silica.

Compounds which can be utilized to
incorporate titanium and zirconium metal with the
support include titanates and zirconates of the
formula

20
$$(R)_nMe(OR)_m$$

where Me is titanium or zirconium; R is a hydrocarbon
radical selected from alkyl, cycloalkyl, aryl, aralkyl
or alkaryl having from 1-12 carbon atoms; m is an
integer from 1 to 4, n is an integer from 0 to 3 and m
25 plus n is equal to 4; and titanium or zirconium
halides of the formula



where Me is titanium or zirconium and X is chlorine,
bromine, fluorine or iodine. Compounds of the above
30 types wherein R is a C₁₋₇ alkyl group and X is
chlorine are particularly useful. In an even more

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-13-

1 advantageous embodiment of the invention the titanium
and zirconium compounds are represented by the formula

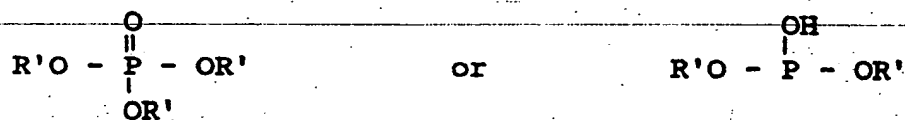


where Me is the same as defined above and R_1 is a C_{1-7}
5 alkyl group, for example, tetraethyl titanate,
tetrakispropyl titanate, tetrakispropyl zirconate,
tetrabutyl titanate, etc. These latter compounds,
also sometimes referred to as titanium tetraethoxide,
titanium tetrakispropoxide, zirconium
10 tetrakispropoxide and titanium tetrabutoxide,
respectively, are conveniently deposited on support
materials by deposition from hydrocarbon solutions.
Tetrakispropyl titanate and tetrakispropyl
zirconate are especially preferred.

15 Titanium and zirconium acetylacetonate
compounds, such as titanyl acetylacetonate and
titanium diacetylacetonate diisopropylate, can also be
used to deposit these metals.

20 Boron is conveniently deposited utilizing an
alkyl ester of boron wherein the alkyl group contains
from 1 to 7 carbon atoms, such as trimethyl borate and
triisopropyl borate, or a halide of boron.

Phosphorus compounds which can be used to
effect deposition are most commonly phosphate esters
25 which correspond to the formulas



30 where R is a hydrocarbon radical selected from alkyl,
cycloalkyl, aryl, aralkyl and alkaryl having from 1 to
12 carbon atoms. Trialkyl phosphates where the alkyl

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-14-

1 group contains from 1 to 7 carbon atoms, such as triethyl phosphate, are particularly useful.

~~The first and second components which~~
5 comprise the mixed catalysts of the invention are obtained by depositing the chromium-containing compound and any additional catalytic agents on the silica support in accordance with conventional known procedures, e.g., vapor coating or deposition from
10 inert organic solvents. Organic solvents which can be employed for this purpose typically include hydrocarbons and their halogenated derivatives. Dichloromethane has been found to be a particularly effective solvent for depositing chromium and aluminum compounds on the supports.

15 The same or different chromium-containing compounds may be used for preparation of the first and second catalyst components. When preparing catalyst components having chromium and one or more other elements the order of deposition may be varied where
20 separate steps are employed. Furthermore, after the first deposition the support having the metal deposited thereon may be heat activated before proceeding with subsequent depositions.

25 In general, the first and second catalyst components can contain from about 0.1 to 2.0 weight percent chromium. More usually, however, the amount of chromium will range from 0.2 to 1.5 weight percent and in a particularly useful embodiment from 0.5 to 1.25 weight percent. Additional metal and nonmetal
30 catalytic agents will be present from 0.1 to 6.0 weight percent and, more preferably, from 0.2 to 4.0 weight percent.

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-15-

1 More specifically, when a metallic catalytic
agent is employed in conjunction with the chromium,
such as when titanium, zirconium or aluminum are
present, these metals will constitute from 0.5 to 6.0
5 weight percent and, more preferably, 1.0 to 4.0 weight
percent of the catalyst component. Nonmetallic
cocatalytic agents, when present on either the first
or second catalyst component, will generally range
from 0.1 to 1.5 weight percent and, more usually, from
10 0.2 to 1.0 weight percent. In a highly useful
embodiment of the invention, the first catalyst
component contains from 0.5 to 1.2 weight percent
chromium, the second catalyst component contains from
0.75 to 1.25 weight percent chromium, and aluminum is
15 associated with the first higher pore volume catalyst
component and is present in an amount from 2 to 4.5
weight percent. In all of the foregoing instances,
the recited weight percentages are based on the total
weight of the catalyst component.

20 The first and second catalyst components
comprising the mixed catalyst compositions of this
invention are thermally activated by heating at a
temperature below the decomposition temperature of the
support material in a non-reducing atmosphere. The
25 heat activation may be carried out before the first
and second catalyst components are combined or after
the first and second catalyst components have been
combined. Temperatures generally employed for this
activation range from about 450°F up to about 1700°F
30 but higher activation temperatures can be utilized
provided the decomposition temperature of the support
material is not exceeded. When the first and second
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-16-

1 catalyst components are combined and co-activated by
heating the mixture of the catalyst, temperatures from
about 950°F to 1500°F are preferably used. ~~When the~~
first and second catalyst components are separately
5 heat activated, temperatures from 950°F to 1650°F are
most advantageously employed. In the latter
situation, the catalyst components may be heat
activated at different temperatures within the above-
recited range. Also, multiple heat activation steps
10 may be carried out. For example, after the first
compound is deposited on the support and before
proceeding with deposition of the second a heat
activation operation may be carried out. Similarly,
after deposition of the second compound, a second heat
15 activation operation may be conducted or the catalytic
material may be directly combined with the other
catalyst component and this mixture then heat
activated.

A non-reducing atmosphere, preferably, an
20 oxygen-containing atmosphere is necessarily employed
for thermal activation. The time required will vary
but generally ranges from about 30 minutes up to about
24 hours and, more preferably, from 2 to 12 hours. If
the first and second catalyst components are
25 separately heat activated, the temperatures employed
and times of activation may be different for each.
The non-reducing atmosphere, which is preferably air
or other oxygen-containing gas, should be essentially
dry. When air is used, it is preferably dehumidified
30 to less than 3 ppm water.

In a particularly useful embodiment of this
invention, the thermal activation is preceded by

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-17-

1 heating the individual catalyst components or the
mixed catalyst composition at a temperature from about
575°F to 1650°F in a reducing atmosphere for a period
of time which can range from several minutes up to
5 several hours. Preferably the reducing atmosphere
consists of a mixture of an inert gas with a reducing
gas. Such procedures are described in U.S. Patent No.
4,041,224. Preferably, the inert gas is nitrogen and
the reducing gas is carbon monoxide and the
10 temperature is between about 1000°F and 1400°F.
Following this reductive treatment step, the catalyst
is then subjected to thermal treatment in the non-
reducing gas in accordance with the previously
described procedure. Where a reducing step is
15 employed prior to activation in a non-reducing
atmosphere, the latter step is preferably carried out
at a temperature from about 800°F to 1100°F.

The mixed catalysts of the invention are
effective to polymerize olefins by themselves or in
20 combination with metallic and/or non-metallic reducing
agents. Examples of metallic reducing agents which
can be used include trialkyl aluminums, such as
triethyl aluminum and triisobutyl aluminum, alkyl
aluminum halides, alkyl aluminum alkoxides, dialkyl
25 zincs, dialkyl magnesiums, and borohydrides including
those of the alkali metals, especially sodium, lithium
and potassium, and aluminum. Non-metal reducing
agents which can be used include alkyl boranes such as
triethyl borane, triisobutyl borane, and trimethyl
30 borane and hydrides of boron such as diborane,
pentaborane, hexaborane and decaborane. The mixed
catalyst may be combined with the metallic or non-

-18-

1 metallic reducing agent prior to being fed to the
polymerization vessel or the mixed catalyst and
reducing agent may be separately fed to the
polymerization reactor. The molar ratio of the metal
5 or non-metal of the reducing agent to chromium can
range from 0.01:1 to 10:1 and more preferably, is in
the range 0.01:1 to 5:1. In a particularly
advantageous embodiment, the molar ratio of metal or
non-metal to chromium is from 0.01:1 to 2:1.

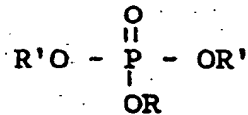
10 In one embodiment of the invention
particularly useful polyethylene resins having a good
balance of physical and rheological properties useful
for the manufacture of blow molded bottles are
produced utilizing a mixed catalyst composition
15 wherein the first catalyst component contains from 0.5
to 1.2 weight percent chromium and from 0.2 to 1.0
weight phosphorus obtained by depositing an
organophosphoryl chromium compound and 2 to 4.5 weight
percent aluminum obtained by depositing an aluminum
20 alkoxide compound, said compounds being deposited on a
silica support having a pore volume from 2.1 cc/g to
2.9 cc/g. It is especially advantageous if the high
pore volume silica support is calcined at 1200°F to
1700°F prior to deposition of the chromium and
25 aluminum compounds.

Chromium/aluminum-containing catalysts of
this type are known and described in U.S. Patent No.
3,984,351, details of which are incorporated herein by
reference. In general, they are obtained by
30 depositing an organophosphoryl chromium compound which
is the reaction product of chromium trioxide and an
organophosphorus compound of the formula

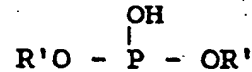
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-19-

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or



wherein at least one of the R' groups is a hydrocarbon radical selected from alkyl, cycloalkyl aryl, aralkyl, or alkaryl. Any R' groups which are not hydrocarbon radicals are hydrogen. Preferred organophosphorus compounds are trialkyl phosphates such as triethyl phosphate. The aluminum alkoxide compounds correspond to the formula

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where R'' is an alkyl having from 1 to 8 carbon atoms or aryl, aralkyl, or alkaryl having from 6 to 8 carbon atoms. Aluminum sec-butoxide, aluminum isopropoxide, aluminum ethoxide, and aluminum phenoxide are representative aluminum alkoxides and aluminum sec-butoxide is particularly advantageous.

15

Especially advantageous results are obtained when the above-described first catalyst component is used in conjunction with a second catalyst component containing from 0.75 to 1.25 weight percent chromium obtained by depositing a chromate ester on a microspheroidal silica support having a pore volume from 1.6 cc/g to 1.8 cc/g. Chromium acetate is a particularly useful chromate ester. Synthetic microspheroidal (amorphous) silica xerogels

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impregnated with chromium acetate are commercially available, e.g., EP30 Polyolefin Catalyst from Crosfield Catalysts. It is even more desirable if a trialkyl borane reducing agent is included in the polymerization with the above-described components and

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-20-

1 when the molar ratio of the boron of the reducing
agent to chromium ranges from 0.1:1 to 1.5:1.

5 In another highly useful embodiment the
above-described higher pore volume catalyst component
contains chromium and titanium and, optionally,
phosphorus. These catalyst components are effective
when employed in conjunction with the above-described
second catalyst components obtained by depositing
chromium acetate on microspheroidal silica but are
10 particularly advantageous when used with a catalyst
component based on the lower pore volume support and
having titanium or zirconium deposited with the
chromium. In an even further and more preferred
embodiment, mixed catalyst compositions which contain
15 zirconium or titanium by virtue of having these metals
deposited with the chromium on either the first or
second catalyst component are thermally activated
utilizing the two step procedure wherein the catalyst
is first heated in a reducing atmosphere of carbon
20 monoxide and subsequently in a non-reducing atmosphere
of air. When zirconium and/or titanium are employed
they are generally present from about 2 to 4 weight
percent and if phosphorous is employed it generally is
present from about 0.1 to 1.0 weight percent.

25 While the catalyst compositions of the
present invention find general utility for the
polymerization of olefins to produce homopolymers and
copolymers in the density range 9.10 to about 9.70,
they are most advantageously employed for the
30 preparation of ethylene homo- and copolymer resins
which have a desirable balance of rheological and
physical properties making them useful for blow

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-21-

1 molding applications. Resins produced in accordance
with the invention are primarily used for blow molding
bottles, especially detergent bottles, bleach bottles
and milk bottles, but can also be used for the
5 production of larger articles such as blowmolded drums
and tanks. Resins obtained using the present improved
mixed catalyst compositions are also useful for films.
For example, high molecular weight film resins
suitable for grocery sacks and merchandise bags and
10 medium molecular weight resins for use in cereal
liners and snack packs can also be produced using the
mixed catalysts of the invention.

Utilizing the above-described preferred
mixed catalysts, it is possible to produce highly
15 processable, high density polyethylene resins which
have high resistance to environmental stress cracking.
For example, polyethylene resins having densities in
the range 0.958 to 0.961 and ESCRs greater than 10
hours with melt indexes in the blowmolding range of
20 0.1 to 0.7 and melt index ratios from 80 to 125 are
readily produced. By judicious selection of the
various catalyst parameters discussed above it is
possible to produce resins having acceptable stiffness
with melt indexes from 0.2 to 0.4 and to achieve even
25 further broadening of the molecular weight
distribution, i.e., higher MIRs. In some instances
the production of bimodal resins is even possible. It
is an especially desirable feature of this invention
that these aforementioned highly useful polyethylene
30 resin products can be obtained using mixed catalysts
without the necessity of separately heat activating
the first and second catalyst components. This

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-22-

1 feature is an extremely useful and beneficial aspect
of the invention from a commercial point of view since
it eliminates ~~a step in the catalyst preparation.~~

5 The mixed catalyst compositions can be used
in virtually any polymerization procedure where
supported catalysts are utilized. This includes both
gas phase (fixed and fluidized bed) polymerizations
and solution polymerizations. They are, however,
10 primarily used for the polymerization of ethylene in
conventional particle form (slurry) processes. Such
procedures are well known and are described in the
prior art, e.g., U.S. Patent No. 3,644,323. In
general these polymerizations are carried out in a
15 liquid organic medium at a temperature from about
150°F to 230°F. The catalyst is suspended in the
organic medium and the reaction is conducted at a
pressure sufficient to maintain the organic diluent
and at least a portion of the olefin in the liquid
phase. Weight percent ethylene in the reactor is
20 generally maintained from about 1.5 up to about 7.
Hydrogen is generally added to the polymerization
reaction for molecular weight control. The molar
ratio of hydrogen to ethylene in the reactor is
generally maintained between 0.25 and 1.0. While not
25 necessary for polymerization, a metallic or non-
metallic reducing agent of the type previously defined
is generally included in polymerizations with the
mixed catalysts of this invention.

30 The organic medium employed for the
polymerization is generally a paraffinic and/or
cycloparaffinic material such as propane, butane,
isobutane, pentane, isopentane, cyclohexane,

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-23-

1 methylcyclohexane, and the like. The medium is chosen
so that under the conditions employed the polymer is
insoluble in the medium and is readily recoverable in
the form of solid particles. Isobutane is a
5 particularly advantageous organic medium for the
purpose of these polymerizations. Pressures typically
range from about 100 to 800 psig and catalyst
concentrations can range from about 0.001 to about 1
10 percent, based on the total weight of the reactor
contents. These slurry polymerizations can be
conducted as batch, continuous or semi-continuous
operations.

The following examples illustrate the
invention more fully. They demonstrate the ability to
15 produce a wide range of readily processable
polyethylene resins having high densities and high
resistance to environmental stress cracking. Unless
otherwise indicated, all parts and percentages are on
a weight basis.

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-24-

EXAMPLE I

1 A mixed catalyst was prepared in accordance
with the present invention and utilized for the
polymerization of ethylene. The catalyst consisted of
5 a mixture of a supported chromium/aluminum catalyst
prepared in accordance with the procedure of U.S.
Patent No. 3,984,351, identified as Catalyst Component
A, and a supported chromium catalyst obtained from
commercial sources, identified as Catalyst Component
10 B.

Catalyst Component A was prepared by
calcining a high pore volume silica support at 1650°F
for 6 hours and thereafter impregnating first with the
reaction product of CrO₃ and triethyl phosphate and
15 then with aluminum sec-butoxide. Impregnations were
made by deposition from dichloromethane solutions.
The impregnated catalyst was then activated by placing
it in a cylindrical container and fluidizing with dry
air at 0.2 feet per minute lineal velocity while
20 heating at 1070°F for 6 hours. The resulting heat-
activated catalyst had a pore volume of 2.3 cc/g and
contained 1.0% chromium, 3.7% aluminum, and 0.6%
phosphorus.

Catalyst Component B was a commercially
25 obtained microspheroidal silica xerogel impregnated
with chromium acetate which was activated by
fluidizing with dry air at 0.2 feet per minute lineal
velocity and heating at 1000°F for 6 hours. The
resulting heat-activated chromium catalyst had a pore
30 volume of 1.7 cc/g and contained 1.0% chromium.
Catalyst Components A and B were blended at a weight
ratio of 3:1 to obtain the mixed catalyst.

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-25-

1 Polymerization was carried out in a jacketed
loop-type reactor provided with an agitator to cause
circulation within the loop and create highly
turbulent flow. Isobutane was employed as the
5 hydrocarbon reaction medium. Means were provided to
continuously feed isobutane, ethylene, a slurry of the
mixed catalyst in isobutane, a solution of triethyl
boron in isobutane and hydrogen to the reactor and for
10 removing a mixture of the polymer, unreacted monomer,
and diluent at a controlled rate. Polymerization
details were as follows:

Temperature (°F)	213
Catalyst Concentration (g/kg isobutane)	0.38
Ethylene in Reactor (%)	3.19
15 H ₂ /Ethylene Molar Ratio	0.49
Boron/Chromium Molar Ratio	0.24

After removal of ethylene and isobutane a
free-flowing polyethylene powder having a density of
0.9599 and ESCR of 10.1 hours per ASTM D-2561,
20 Procedure C was obtained. The resin had an MI of 0.26
and MIR of 119 and was readily fabricated using
conventional blowmolding equipment into blown bottles.

The above polymerization was repeated except
that the conditions were varied as follows:

25 Temperature (°F)	212
Catalyst Concentration (g/kg isobutane)	0.40
Ethylene in Reactor (%)	2.97
H ₂ /Ethylene Molar Ratio	0.49
Boron/Chromium Molar Ratio	0.25

30 The resulting polyethylene resin had a density of
0.9595, ESCR of 10.5 hours, MI 0.20, and MIR of 122.

-26-

1 A useful high density resin was obtained
even when the mixed catalyst was employed without
triethyl borane reducing agent. ~~For example, when~~
ethylene was polymerized at 214°F using a catalyst
5 concentration of 0.73 g/kg isobutane with 3.81 weight
percent ethylene and H₂/ethylene molar ratio of 0.35,
a resin having a density of 0.9601, ESCR of 8.9 hours,
MI of 0.26, and MIR of 130 was obtained. While the
environmental stress crack resistance of the resin was
10 somewhat lower than that obtained when triethyl borane
is used, it nevertheless is considered to be within
acceptable limits.

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EXAMPLE II

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To further demonstrate the ability to obtain high density resins having increased environmental stress crack resistance, a mixed catalyst was prepared by blending Catalyst Components A and B of Example I at a weight ratio of 1:1. The catalyst was employed for the polymerization of ethylene in accordance with the procedure of Example I under the following conditions:

10

Temperature (°F)	212
Catalyst Concentration (g/kg isobutane)	0.41
Ethylene in Reactor (%)	2.17
Hydrogen/Ethylene Molar Ratio	0.89

15

The resulting polyethylene resin had a density of 0.9601 and ESCR of 11.4 hours. The MI and MIR of the resin were 0.26 and 110, respectively.

20

When the polymerization was repeated increasing the ethylene in the reactor to 2.82% and lowering the hydrogen/ethylene molar ratio to 0.69, a resin of density 0.9606, ESCR of 10.1 hours, MI of 0.24, and MIR of 118 was obtained.

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-28-

EXAMPLE III

A chromium/aluminum/phosphorus catalyst, identified as Catalyst Component C, was prepared as described for Catalyst Component A in Example I except that the high pore volume silica support was not calcined prior to deposition of the chromium and aluminum compounds. After deposition of the chromium and aluminum compounds, Component C was air-dried and combined at a 1:1 weight ratio with a commercial chromium acetate impregnated microspheroidal silica xerogel (1.0% Cr; pore volume 1.7 cc/g). The mixture was then co-activated by fluidizing the mixture with dry air at 0.2 feet per minute lineal velocity and heating at 1100°F for 6 hours. The resulting heat-activated mixed catalyst was employed for the polymerization of ethylene. Polymerization conditions and properties of the resulting resin-produced thereby were as follows:

Temperature (°F)	218
Catalyst Concentration (g/kg isobutane)	0.40
Ethylene in Reactor (%)	4.0
H ₂ /Ethylene Molar Ratio	0.28
Boron/Chromium Molar Ratio	0.14
Density	0.9592
ESCR (hours)	12
MI	0.23
MIR	113

It is evident from the foregoing data that the product produced in accordance with the above-defined polymerization conditions has an excellent balance of physical and rheological properties which make it useful for blow molding applications. when

-29-

1 the above-defined catalyst components are individually
employed for the polymerization of ethylene under
comparable polymerization conditions, resins having
~~the desired balance of physical and rheological~~
5 properties are not produced. For example, when high
density resins having acceptable rheological
properties are obtained, the stress crack resistance
of the polymers is deficient.

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EXAMPLE IV

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To demonstrate the significant improvement obtained with the mixed catalyst compositions of this invention, polyethylene resin produced using a mixed catalyst was compared with resins produced using the individual catalyst components.

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A supported catalyst containing chromium, aluminum and phosphorus was prepared in accordance with the general procedure described for Catalyst Component A in Example I using a high pore volume silica support (2.24 cc/g). The high pore volume silica was dried at 550°F for two hours prior to deposition and then impregnated first with the reaction product of CrO₃ and triethyl phosphate and then with aluminum sec-butoxide. The depositions were made from dichloromethane solutions in accordance with the procedure described in U.S. Patent No. 3,984,351. After drying the resulting supported catalyst (identified as IV(a)) had the following analysis: 0.90% Chromium; 3.70% Aluminum; and 0.54% phosphorus.

25

A supported catalyst containing chromium on a lower pore volume silica and corresponding to catalyst component B in Example I was employed as the second catalyst component and identified as IV(b). The catalyst was a commercially available microspheroidal silica xerogel impregnated with chromium acetate (1.0% Cr) purchased from Davison Chemical Division, W.R. Grace & Co. under the designation MS-952.

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To obtain the mixed catalyst components IV(a) and IV(b) were combined in equal weight proportions and blended by fluidizing with dry air at

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-31-

1 0.2 feet per minute lineal velocity. The resulting
mixed catalyst, identified as IV(mc), was not analyzed
since the metal values and pore volume are one-half of
the sum of the values of the individual catalyst
5 components.

Each of the above catalysts IV(a), IV(b),
and IV(mc), was used to polymerize ethylene in the
particle form polymerization process. Prior to
polymerization each catalyst was heat-activated in a
10 non-reducing atmosphere in accordance with the general
practice, i.e., by fluidizing with dry air at 0.2 feet
per minute lineal velocity and heating for a specified
time. Conditions employed for the heat activation and
polymerization with each of the above catalysts were
15 selected to produce polyethylene resins suitable for
blow molding having comparable densities (greater than
0.957) and comparable MIs (in the preferred range of
0.1 to 0.4). Polymerizations were then carried out in
a production-scale jacketed loop reactor which was
20 highly agitated to create circular highly turbulent
flow within the loop. Isobutane was employed as the
hydrocarbon reaction medium and, in accordance with
the preferred practice for this type of
polymerization, a co-catalyst (triethyl borane) and
25 modifier (hydrogen) were employed. Heat activation
details, polymerization details and properties of the
polyethylene resins produced with each catalyst were
as follows:

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-32-

	CATALYST IV(a)	CATALYST IV(b)	CATALYST IV(mc)
1			
	Heat Activation:		
5	Temp. (°F)	1200	1600 ¹
	Time (hours)	6	6
	Polymerization:		
10	Temp. (°F)	214	224
	Press (psig)	650	650
	Catalyst Conc. (g/kg isobutane)	0.40	0.38
15	C ₂ H ₄ in Reactor (wt.%)	3.2	3.5
	H ₂ /C ₂ H ₄ Molar Ratio	0.36	0.08
	B/Cr Molar Ratio	0.19	0.42
20	% Solids	41	39
	Polyethylene Resin:		
	Density	0.9595	0.9596
	MI (pellet)	0.36	0.34
25	MIR	95.5	98.5
			107.7

¹High activation temperature is required with this catalyst to produce a resin with MI in the desired range.

-33-

1 Standard blow molded containers (shampoo
bottles) were produced using each of the above-
identified resins and evaluated for environmental
~~stress-crack resistance in accordance with modified~~
5 ASTM D-2561, Procedure C, Controlled Elevated Pressure
Stress-Crack Resistance of a Specific Container to
Polyoxyethylated Nonylphenol, a Stress-Cracking Agent.
In this test the internal pressure is controlled at a
constant elevated level. The shampoo bottles blow
10 molded from the resins produced using Catalysts IV(a)
and IV(b) failed after 8.5 and 10.5 hours,
respectively, whereas the bottles formed from the
resin produced using mixed catalyst IV(mc) ran for
19.8 hours before failure.

15 Blown containers produced using the above-
identified polyethylene resins were also evaluated for
column crush properties in accordance with ASTM D
2659-84. This test determines the mechanical
properties of blown thermoplastic containers when
20 loaded under columnar crush conditions at a constant
rate of compressive deflection. For this evaluation
the specimens tested were bleach bottles blow molded
using 25 ± 0.10 grams of the resin. Results were as
follows:

25

Resin Produced
Using

	<u>CATALYST IV(a)</u>	<u>CATALYST IV(b)</u>	<u>CATALYST IV(mc)</u>
Crushing Load at Failure (lbs)	57.5	57.2	63.2

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It is apparent from the above data that the
increased column crush value obtained with the resin
produced using the mixed catalyst IV(mc) would make it

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-34-

1 possible to lightweight the bleach bottles by 10 to 15 percent.

5 To further demonstrate the versatility of the invention and the ability to vary the catalyst components, a series of experiments were conducted using different mixed catalysts and are reported in the examples which follow. Catalyst components used to prepare the mixed catalysts referred to in Examples V-XII were as follows:

10 Catalyst Component A: As described in Example I containing 1.0% Cr, 0.6% P and 3.7% Al.

Catalyst Component B: As described in Example I containing 1.0% Cr.

15 Catalyst Component D: A commercially available chromium-containing catalyst (EP30 from Crosfield Catalysts - chromium acetate on silica having a pore volume of 1.6 cc/g) was additionally impregnated with boron. The boron was incorporated by adding trimethylborate to a slurry of chromium-containing catalyst in methylene chloride and evaporating the solvent. Chromium and boron contents were 1.0% and 1.2%, respectively.

20 Catalyst Component E: Titanium was incorporated on the chromium-containing silica used for Catalyst Component D. Deposition was accomplished in the usual manner using tetrapropyltitanate and methylene chloride as the solvent. After drying, the catalyst component was analyzed and found to contain 1.0% Cr and 3.7% Ti.

25 Catalyst Component F: Silica (pore volume 2.3 cc/g) was calcined at 1650°F for 6 hours and impregnated with the reaction product of CrO₃ and triethyl

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-35-

1 phosphate. Titanium was then deposited utilizing the
slurry technique with tetrapropyltitanate and
methylene chloride. Analysis of the dried catalyst
component showed it to contain 1.0% Cr, 0.69% P and
5 3.7% Ti.

Catalyst Component G: A high pore volume silica (2.3
cc/g) was calcined and chromium acetylacetonate
deposited thereon. Titanium was then deposited as for
Catalyst Component F to obtain a catalyst containing
10 1.0% Cr and 3.7% Ti.

Catalyst Component H: The commercial chromium-
containing catalyst employed for Catalyst Component D
was additionally impregnated with aluminum using
aluminum sec-butoxide and methylene chloride. The
15 catalyst contained 1.0% Cr and 3.7% Al.

Catalyst Component I: The commercial chromium-
containing catalyst employed for Catalyst Component D
was modified with zirconium. The modification was
accomplished by adding triisopropyl zirconate to a
20 slurry of the chromium-containing catalyst in
methylene chloride and evaporating the solvent.
Chromium and zirconium contents were 1.0% and 3.7%,
respectively.

Polymerizations for Examples V-XII were
25 conducted in a one-liter autoclave equipped with a
mechanical overhead stirrer and an external jacket for
regulating temperature. The polymerization was
performed by providing the continuous addition of
ethylene at a fixed total pressure. The reactor had
30 thermocouples to control the temperature of the
external jacket and the internal temperature of the
reactor during the polymerization. Ethylene fed to

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-36-

1 the reactor was passed through an electronic gas flow
meter to permit continuous monitoring of the ethylene
flow to the reactor. All handling of the
polymerization reaction components was carried out
5 using airless techniques to exclude oxygen and water.
The polymerizations were conducted in a slurry of
isobutane which had been dried and deoxygenated. The
autoclave was charged first with catalyst and then
10 with 450 ml isobutane. The autoclave was then heated
and the introduction of ethylene was commenced when
the desired temperature was reached.

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-37-

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EXAMPLE V

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A mixed catalyst was prepared by combining Catalyst Component A (high pore volume) and Catalyst Component D (low pore volume) at a weight ratio of 1:1. The mixture was then activated by fluidizing with dry air at 2 feet per minute lineal velocity and heating at 1200°F for 6 hours. The resulting mixed catalyst thus obtained was then evaluated for its ability to polymerize ethylene in accordance with the procedure described above. Two polymerizations, identified as Run A and Run B, were made and the conditions employed for each and results obtained were as follows:

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	Run A	Run B
Temperature (°F)	221	221
Other Pzn Variables	8.5	8.5
Polymer Recovered (grams)	150	124
Productivity ¹	1194	2094
Activity ²	3256	2417
Resin Properties:		
Density	.9554	N.D. ³
MI	0.48	0.092
HLMI	35.9	11.5
MIR	74.8	124.6

¹ Grams polymer per gram of catalyst

² Grams polymer per gram of catalyst per hour

³ N.D. = not determined

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-38-

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EXAMPLE VI

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Three mixed catalysts were prepared by combining Catalyst Component A and Catalyst Component E at different weight ratios and used to polymerize ethylene. The mixed catalysts were activated at 1100°F for 6 hours in air. Compositions of the mixed catalysts, details of the polymerizations and properties of the resins produced were as follows:

10		Run A	Run B	Run C
	Wt. Ratio A:E	1:1	4:1	1:4
	Temperature (°F)	221	221	221
	Ethylene in Reactor (wt.%)	8.5	8.5	8.5
15	Polymer Recovered (grams)	72	142	131
	Productivity	1283	2178	2060
	Activity	1426	2513	2247
	Resin Properties:			
20	Density	.9598	.9591	.9628
	MI	.74	.19	1.14
	HLMI	58.1	16.9	77.6
25	MIR	78.5	88.7	68.1

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-39-

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EXAMPLE VII

5 A mixed catalyst containing chromium, phosphorus and titanium was prepared by combining Catalyst Component ~~P~~ and Catalyst Component ~~B~~ at a 1:1 wt. ratio. Two polymerizations were conducted using the mixed catalyst. For the first polymerization (Run A) the mixed catalyst was activated by heating in air at 1200°F for 6 hours and for the second polymerization (Run B) the catalyst was activated in air at 1100°F for six hours. Results were as follows:

10

	Run A	Run B
Temperature (°F)	221	221
15 Ethylene in Reactor (wt.%)	8.5	8.5
Polymer Recovered (grams)	138	135
Productivity	1618	2292
Activity	2489	2547
20 Resin Properties:		
Density	N.D.	.9548
MI	0.43	0.21
HLMI	36.8	16.3
25 MIR	85.6	77.7

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EXAMPLE VIII

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Mixed catalysts containing chromium, titanium, and aluminum obtained by combining higher pore volume based Catalyst Component G with lower pore volume based Catalyst Component H were prepared, activated in air at 1100°F in the usual manner and evaluated for the polymerization of ethylene. Results were as follows:

10		Run A	Run B
	Wt. Ratio G:H	1:1	4:1
	Temperature (°F)	221	221
	Ethylene in Reactor (%)	8.5	8.5
15	Polymer Recovered (grams)	112	128
	Productivity	2171	1960
	Activity	2368	2330
	Resin Properties:		
20	Density	.9595	.9606
	MI	0.68	1.10
	HLMI	46.1	77.0
25	MIR	67.8	70

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-41-

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EXAMPLE IX

Mixed catalysts containing chromium, titanium, and boron were obtained by combining

~~Catalyst Component G with Catalyst Component D.~~ The mixed catalysts were activated at 1200°F in the usual manner and used to polymerize ethylene. Results were as follows:

		Run A	Run B
10	Wt. Ratio G:D	2:1	1:1
	Temperature (°F)	221	221
	Ethylene in Reactor (%)	8.5	8.5
	Polymer Recovered (grams)	132	114
15	Productivity	1803	1344
	Activity	3381	1753
	Resin Properties:		
20	Density	N.D.	.9585
	MI	1.0	1.25
	HLMI	58.1	90.9
	MIR	58.1	72.7
25			

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-42-

EXAMPLE X

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To further demonstrate the versatility of the invention and the ability to vary resin properties by changing the activation conditions, the following experiment was conducted. For this example the mixed catalyst of Example VI, comprised of a mixture of one part Catalyst Component A (chromium, aluminum and phosphorous on higher pore volume silica) and one part Catalyst Component E (chromium and boron on lower pore volume silica), was activated utilizing a multiple step procedure. The activation procedure entailed: (a) heating the mixed catalyst to approximately 300°F under nitrogen over a one hour period; (b) maintaining the mixed catalyst at 300°F for two hours under nitrogen; (c) gradually increasing the temperature of the mixed catalyst to 1290°F over a 6 hour period under an atmosphere of carbon monoxide and nitrogen (wt. ratio 3:97); (d) maintaining the mixed catalyst at 1290°F for 6 hours under the CO/N₂ atmosphere; (e) cooling the mixed catalyst to 930°F over a 2 hour period under nitrogen; (f) heating the mixed catalyst for one hour in air at 930°F; and (g) cooling the mixed catalyst to ambient temperature over a period of 5 hours under nitrogen. The total time required for this activation procedure was 23 hours.

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The mixed catalyst activated in the above manner was employed for the polymerization of ethylene. Polymerization conditions and properties of the resulting resin were as follows:

-43-

1		Run A	Run B
	Temperature (°F)	214	201
5	Ethylene in Reactor (%)	5	5
	Polymer Recovered (grams)	93	119
	Productivity	1970	1653
	Activity	1970	1417
10	Resin Properties:		
	Density	.9619	.9625
	MI	0.52	0.08
	HLMI	45.8	11.8
15	MIR	88	147.5

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-44-

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EXAMPLE XI

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Utilizing the activation procedure of Example X, a mixed catalyst obtained by combining two parts Catalyst Component A with one part Catalyst Component B was prepared and used to polymerize ethylene. Results were as follows:

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Temperature (°F) 212

Ethylene in Reactor (%) 5

Polymer Recovered (grams)

Productivity 1918

Activity 2131

Resin Properties:

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Density .9604

MI 0.105

HLM 17.8

MIR 169.5

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EXAMPLE XII

A mixed catalyst containing chromium, aluminum, phosphorus and zirconium was prepared by combining catalyst component A and catalyst component

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I at a 1:1 ratio. The mixed catalyst was then activated following the procedure of Example X and employed for the polymerization of ethylene. Polymerization conditions employed and resin properties were as follows:

10

Temperature (°F) 212

Ethylene in Reactor (%) 5

Polymer Recovered (grams) 102

Productivity 1977

Activity 2118

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Resin Properties:

Density .9603

MI 0.02

HLMI 7.5

MIR 375

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-46-

1 We claim:

5 1. A mixed chromium catalyst composition
~~containing a first and second silica-supported~~
chromium catalyst component; said first and second
catalyst components present at a weight ratio from
10:1 to 1:10 and each containing from 0.1 to 2.0
weight percent chromium with at least one of said
catalyst components containing an additional metallic
or non-metallic element selected from aluminum,
10 titanium, zirconium, boron or phosphorus with the
proviso that when one of the catalytic components
contains chromium and aluminum the other component
shall contain more than one metallic or non-metallic
catalytic element; and the silica supports of said
15 first and second catalyst components differing in pore
volume by at least 0.3 cc/g.

20 2. The mixed chromium catalyst composition
of Claim 1 wherein prior to thermal activation in the
non-reducing atmosphere the first catalyst component,
the second catalyst component or a mixture of the
first and second catalyst components is heated in a
reducing atmosphere at 575°F to 1650°F.

25 3. The mixed chromium catalyst composition
of Claim 2 wherein the reducing atmosphere is a
~~mixture of nitrogen and carbon monoxide.~~

30 4. The mixed chromium catalyst composition
of Claim 1, 2 or 3 wherein the weight ratio of the
first and second catalyst components is from 5:1 to
1:5 and the pore volume of the silica support of the
first catalyst component is greater than 1.0 cc/g and
at least 0.3 cc/g higher than the pore volume of the
silica support of the second catalyst component.

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-47-

1 5. The mixed chromium catalyst composition
of Claim 4 wherein the pore volume of the silica
support of the first catalyst component is from 1.7 to
3.1 cc/g and the pore volume of the silica support of
5 the second catalyst component is from 1.0 to 2.0 cc/g.

6. The mixed chromium catalyst composition
of any of Claims 1 to 5 wherein either or both of the
silica supports employed for the first and second
catalyst components is calcined at a temperature from
10 200°F to 1800°F prior to metal deposition.

7. The mixed chromium catalyst composition
of Claim 3 wherein the metallic or non-metallic
element is present in an amount from 0.1 to 6.0 weight
percent and the first catalyst component, the second
15 catalyst component or a mixture of the first and
second catalyst components is thermally activated by
heating in a non-reducing atmosphere at a temperature
from 450°F to 1700°F.

8. The mixed chromium catalyst composition
20 of any of Claims 1 to 7 wherein the first catalyst
component contains 0.5 to 1.2 weight percent chromium,
14.5 weight percent aluminum and 0.1 to 1.0 weight
percent phosphorus and the second catalyst component
contains 0.75 to 1.25 weight percent chromium.

9. The mixed chromium catalyst composition
25 of Claim 8 wherein 2 to 4.5 weight percent titanium or
zirconium is additionally present.

10. The mixed chromium catalyst composition
of Claim 9 wherein the titanium is associated with the
30 first catalyst component.

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-48-

1 11. The mixed chromium catalyst composition
of any of Claims 1 to 10 wherein a metallic or non-
metallic reducing agent is present and the molar ratio
5 of the metal or non-metal of said reducing agent to
chromium ranges from 0.01:1 to 5:1.

10 12. The mixed chromium catalyst composition
of Claim 9 wherein the metallic or non-metallic
reducing agent is selected from the group consisting
of trialkyl aluminums, alkyl aluminum halides, alkyl
aluminum alkoxides, dialkyl zincs, dialkyl magnesiums,
alkali metal borohydrides, aluminum borohydrides,
alkyl boranes, and boron hydrides.

15 13. The mixed chromium catalyst composition
of Claim 12 wherein the reducing agent is triethyl
borane.

20 14. In a process for the particle form
polymerization of ethylene, to produce high density
resins useful for blow molding with broadened
molecular weight distributions, the improvement
comprising conducting the polymerization in the
presence of a mixed catalyst set forth in any of
Claims 1 to 13.

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INTERNATIONAL SEARCH REPORT

International Application No. PCT/US92/02337

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³ According to International Patent Classification (IPC) or to both National Classification and IPC IPC (5): C08F 4/648, C08F 4/69, C08F 4/646 US CL : 502/113; 526/106																										
II. FIELDS SEARCHED <div style="text-align: center; border: 1px solid black; padding: 2px;">Minimum Documentation Searched⁴</div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 20%; padding: 5px;">Classification System</td> <td style="padding: 5px;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">U.S.</td> <td style="padding: 5px;">502/113, 117, 120, 162, 204, 210, 242; 526/105, 106</td> </tr> </table> <div style="text-align: center; border: 1px solid black; padding: 2px;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched⁵</div>			Classification System	Classification Symbols	U.S.	502/113, 117, 120, 162, 204, 210, 242; 526/105, 106																				
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁵ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> </div> </div>																										
IV. CERTIFICATION <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;"> Date of the Actual Completion of the International Search² <div style="text-align: center; font-weight: bold;">30 JUNE 1992</div> </td> <td style="width: 50%; padding: 5px;"> Date of Mailing of this International Search Report² <div style="text-align: center; font-weight: bold;">14 JUL 1992</div> </td> </tr> <tr> <td style="padding: 5px;"> International Searching Authority¹ <div style="text-align: center; font-weight: bold;">ISA/US</div> </td> <td style="padding: 5px;"> Signature of Authorized Officer²⁰ <div style="text-align: center;"> PATRICK P. GARVIN </div> </td> </tr> </table>			Date of the Actual Completion of the International Search ² <div style="text-align: center; font-weight: bold;">30 JUNE 1992</div>	Date of Mailing of this International Search Report ² <div style="text-align: center; font-weight: bold;">14 JUL 1992</div>	International Searching Authority ¹ <div style="text-align: center; font-weight: bold;">ISA/US</div>	Signature of Authorized Officer ²⁰ <div style="text-align: center;"> PATRICK P. GARVIN </div>																				
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FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US, A, 4,560,733 (MARTIN ET AL.) 24 December 1985, See Abstract, col. 2, lines 1-14 & the examples.	1-14
A,P	US, A, 5,081,089 (REKERS ET AL.) 14 January 1992, See Abstract, col. 2, lines 43-66.	1-8, 11, 14

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹

1. ☐ Claim numbers , because they relate to subject matter (1) not required to be searched by this Authority, namely:
2. ☐ Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out (1), specifically:
3. ☐ Claim numbers , because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING²

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Search Authority did not invite payment of any additional fee.

Remark on protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.